

ELECTRON SPIN RESONANCE (ESR) STUDIES OF RETURNED COMET NUCLEUS SAMPLES; Fun-Dow Tsay, Soon Sam Kim, and Ranty H. Liang, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109

INTRODUCTION. The most important scientific objective of the planned Comet Nucleus Sample Return Mission is to return to Earth the least altered, pristine samples which could reflect formation conditions and evolutionary processes in the early solar nebula. It is expected that the returned cometary samples will consist of fine-grained silicate materials mixed to some extent with ices composed of simple molecules such as H_2O , NH_3 , CH_4 as well as organics and/or more complex compounds. Because of the exposure to ionizing radiation from cosmic-ray, gamma-ray and solar wind proton at low temperature, free radicals in the form of $\cdot\text{H}$, $\cdot\text{OH}$, $\cdot\text{CH}_3$ and $-\dot{\text{C}}\text{H}_2$ are expected to be formed and trapped in the solid ice matrices. The kind of trapped radical species together with their concentration and thermal stability can be used as a dosimeter as well as a geothermometer to determine thermal and radiation histories as well as outgassing and other possible alternation effects since the nucleus material was formed. Since free radicals that are known to contain unpaired electrons are all paramagnetic in nature, they can be readily detected and characterized in their native form by the Electron Spin Resonance (ESR) method. In fact, ESR has been shown to be a non-destructive, highly sensitive tool for the detection and characterization of paramagnetic (Fe^{3+} , Ti^{3+} and Mn^{2+}), ferromagnetic (magnetite, hematite and metallic iron), and radiation damage centers in terrestrial and extraterrestrial geological samples (1-6). The purpose of this abstract is to point out the potential use of ESR as an effective method in the study of returned comet nucleus samples, in particular, in the analysis of fine-grained, solid state icy samples.

ESR SPECTROSCOPY. ESR measures the absorption of microwaves by a paramagnetic or ferromagnetic center in the presence of an applied external magnetic field. Conventional ESR experiments are carried out with varying magnetic fields on samples in a tuned resonant cavity operated at a certain frequency. The magnetic field position (g-value) at which resonance occurs, together with the number of resonance lines (fine and hyperfine structure) and the separation between them (zero-field splitting and hyperfine coupling constant), provides a direct identification of magnetic species, their oxidation state and chemical environment. Detailed analyses of ESR signals and their response to physical and chemical treatments can furnish further information on the nature, origin, thermal stability and formation condition of the magnetic species examined. The sensitivity of ESR is such that it can detect 3×10^{12} standard spin (or molecules assuming one spin per molecule). Thus, milligram-size cometary samples can be examined non-destructively as a function of temperature by ESR. In many instances, ESR has the advantage of detailed submicroscopic identification of transient species and/or reaction intermediates generated in UV and/or gamma-ray radiation. We intend to use the unique capability of ESR to investigate the thermal cycling, radiation exposure, shock effects and oxidation/reduction conditions in the formation and evolution of comet nucleus samples.

THERMAL AND RADIATION HISTORIES. Free radicals in the form of $\cdot\text{OH}$ and HO_2 have been detected in γ -irradiated ice at 77°K (see Fig. 1). These free radicals are found to be unstable and to decay rapidly above 110°K as reported (7). No ESR signals of the free radicals can be detected above 160°K. The characteristic ESR signals of $\cdot\text{H}$ having a hyperfine coupling

constant of 500 gauss and present in γ -irradiated ice can only be detected below 60°K (7). ESR studies have also been carried out on γ -irradiated formaldehyde (CH_2O) and UV-irradiated frozen aqueous solutions of glycine ($\text{NH}_2\text{CH}_2\text{COOH}$) at 77°K (see Fig. 1). The thermal and radiation histories as well as the extent of alternation for the returned comet nucleus samples can be determined from the time-temperature-dosage dependence of the ESR signals arising from various free radicals as produced by radiation and trapped in the cometary ice matrices.

SHOCK EFFECTS. The ESR methodology has been developed to determine shock-induced effects on carbonate minerals (5). By studying the ESR spectrum of Mn^{2+} present as impurity in calcite, it is possible to establish the distortion in the crystal structure as a function of shock loading and determine the shock loading history of a sample of unknown history. The lattice distortion caused by shock-induced effects can be effectively quantified through the ESR measurements of zero-field splitting parameters in Mn^{2+} . The characteristic ESR signals of Mn^{2+} in calcite have been detected in C-2 carbonaceous chondrites.

REDOX CONDITIONS. Previous ESR studies have successfully related the annealing temperature and surface exposure parameter to the magnetic properties of very fine lunar metallic Fe phases ubiquitously present (1-3). In addition, no ESR signals attributable to Fe^{3+} have been detected in the returned lunar surface samples, indicating highly reducing conditions prevail on the surface of moon. Recently, ESR has been used to make the first direct measurement of Ti^{3+} in meteoritic and synthetic hibonite (6). The ESR study has further established the use of $\text{Ti}^{3+}/\text{Ti}^{4+}$ ratios as indicators of oxygen fugacity in probing redox conditions in the early solar nebula (6). The ESR detection of the presence or absence of Fe^{3+} , Ti^{3+} and metallic Fe in the returned cometary samples should provide information about the formation conditions of comets and their subsequent evolutionary processes.

REFERENCES: 1. F. D. Tsay, S. I. Chan and S. L. Manatt, *Geochim. Cosmochim. Acta*, **35**, 865 (1971). 2. F. D. Tsay, S. I. Chan and S. L. Manatt, *Nature*, **237**, 77 (1972). 3. F. D. Tsay, S. L. Manatt and S. I. Chan, *Geochim. Cosmochim. Acta*, **37**, 1201 (1973). 4. T. J. Ahrens, F. D. Tsay and D. H. Live, *Proc. Seventh Lunar Sci. Conf.*, 1143 (1976). 5. J. Vizgirda, T. J. Ahrens and F. D. Tsay, *Geochim. Cosmochim. Acta*, **44**, 1059 (1980). 6. J. R. Beckett, D. Live, F. D. Tsay, L. Grossman and E. Stolper, *Geochim. Cosmochim. Acta*, **52**, 1479 (1988). 7. S. Siegel, J. M. Flournoy and L. H. Baum, *J. Chem. Phys.*, **34**, 1782 (1961).

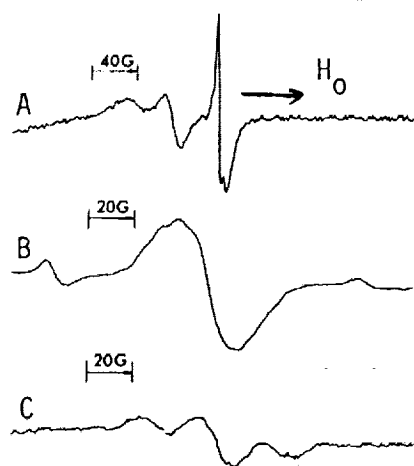


Fig. 1. A. The ESR spectrum observed for the γ -irradiated ice at 77°K. The center and high-field peaks are the doublet of $\cdot\text{OH}$, whereas the broad, low-field peak is due to HO_2 ; the sharp component which is superimposed on the high-field peak of the $\cdot\text{OH}$ doublet is due to the free electron trapped in ice. B. The ESR spectrum of γ -irradiated formaldehyde at 77°K. The low- and high-field peaks are the doublet of $\cdot\text{CHO}$, whereas the broadened center peak is the composite spectrum of the ESR signals arising from multiple radical species ($\cdot\text{CH}_3$, $-\text{O}\dot{\text{C}}\text{HO}-$ and $\cdot\text{OCHO}$); the ESR signals disappear above 210°K. C. The triplet ESR spectrum observed for $-\dot{\text{C}}\text{H}_2$ radicals in the UV-irradiated ice containing 0.2 M glycine at 77°K. The ESR signals decay rapidly at high temperature.